(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 798 372 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
01.10.1997 Bulletin 1997/40

(51) Int. Cl.[6]: **C11D 10/04**, C11D 1/72

(21) Application number: **97200875.9**

(22) Date of filing: **26.03.1997**

(84) Designated Contracting States:
DE ES FR GB IT

(30) Priority: **29.03.1996 EP 96200871**

(71) Applicants:
- **UNILEVER N.V.**
  NL-3000 DK Rotterdam (NL)
  Designated Contracting States:
  DE ES FR IT
- **UNILEVER PLC**
  London EC4P 4BQ (GB)
  Designated Contracting States:
  GB

(72) Inventors:
- **van der Pas, Johannes Cornelis**
  3133 AT Vlaardingen (NL)
- **Brouwn, Lili Faucia**
  3133 AT Vlaardingen (NL)
- **de Vries van Lingen, Caecilia Hedwig E.**
  3133 AT Vlaardingen (NL)

(74) Representative: **Joppe, Hermina L. P.**
Unilever N.V.
Patent Division
P.O. Box 137
3130 AC Vlaardingen (NL)

(54) Detergent composition

(57) The present invention relates to aqueous liquids comprising nonionic surfactants and to a process of preparing such liquids.

EP 0 798 372 A2

Printed by Rank Xerox (UK) Business Services
2.14.15/3.4

Description

Technical field

The present invention relates to aqueous liquids comprising nonionic surfactants and to a process of preparing such liquids.

Background & Prior Art

Liquid detergent compositions are well-known in the art and offer several advantages over solid compositions. For example, liquid compositions are easier to dose, to dispense and to dissolve into a laundering liquor. Further, liquid compositions give more confidence to the consumer of being safer and less harsh to the washed or laundered textile than solid compositions. This may be the reasons why heavy duty and light duty built laundry liquid detergent products are gaining in popularity ever since their introduction on the market at the expense of powdered detergent products.

Two general and separate classes of liquids compositions, isotropic and structured liquids, are known in the art. Isotropic liquids are liquids in which all ingredients are dissolved and, contrary to structured liquids, there is no structure present in isotropic liquid.

Structured liquids are well-known in the art. Structuring may be brought about to endow properties such as consumer preferred flow properties and/or turbid appearance. Many structured liquids are also capable of suspending particulate solids. Examples of structured liquids are given in US 4,244,840, EP 160342, EP 38101 and EP 140452. Structured liquids can either be internally structured, whereby the structure is formed by primary ingredients, preferably by surfactant material, and/or by providing a three dimensional matrix structure using secondary additives, preferably polymers and/or silicate material.

Externally structured liquids may provide a high viscosity upon storage.

Some of the different kinds of liquids, that are internally structuring with surfactant material, are described in the reference H.A. Barnes, "Detergents", Ch.2. in K. Walters (Ed), "Rheometry: Industrial Applications", J. Wiley & Sons, Letchworth 1980. In general, the degree of ordering of such systems increases with increasing surfactant and/or electrolyte concentrations. At very low concentrations of surfactant and/or electrolyte, the surfactant can exist as a molecular solution, or as a solution of spherical micelles, both of these solutions being isotropic, i.e. they are not structured. With the addition of further surfactant and/or electrolyte structures of surfactant material may form. Various forms of such structures exists, e.g. bi-layers. They are referred to by various terms such as rod-micelles, anisotropic surfactant phase, planar lamellar structures, lamellar droplets and liquid crystalline phases. Often different workers have used different terminology to refer to the structures which are really the same. For instance, in European patent specification EP 151884, lamellar droplets are called spherulites.

We have found that detergent compositions comprising nonionic surfactants have a desirable cleaning performance. It is however difficult to incorporate nonionic surfactants in detergent compositions, in particular at higher levels. For instance, in solid compositions nonionic surfactants may lead to so-called bleeding problems. We have found that it is also difficult to prepare liquids comprising nonionic surfactants, in particular at high levels of nonionic surfactants, in view of wicking of the package, viscosity and/or stability problems.

EP 600847 (Procter & Gamble) describes aqueous liquid compositions comprising nonionic surfactants and coconut soap. GB 2,271,574 (Albright & Wilson) discloses single phase compositions comprising soap and nonionic surfactants. DE 28 19 455 (Unilever), EP 42648 (Unilever), DE 41 23 142 (Henkel), DE 40 38 223 (Hüls), DE 41 16 807 (Henkel) and DE 43 44 154 (Henkel) disclose isotropic liquids comprising nonionic surfactants, soap, high hydrotrope levels and low electrolyte levels. DE 43 29 065 (Henkel) discloses isotropic liquids with high water levels. These references disclose compositions comprise high levels of non-functional and expensive hydrotropes. In addition, they do not allow for suspending solid particles.

EP 598693 (Procter & Gamble), EP 634476 (Procter & Gamble) and EP 405967 (Amway Corporation) disclose compositions comprising nonionic surfactants that do not comprise soap.

EP 346993 (Unilever) and EP 346994 (Unilever) describe aqueous liquids comprising nonionic surfactants and high soap levels. The liquids have low surfactant levels, high water levels, contain high anionic surfactant levels and do not contain a deflocculating polymer.

EP 328176 (Unilever) discloses aqueous structured liquid compositions comprising suspended active material which is present in discrete units. The composition may comprise nonionic surfactant. EP 328177 (Unilever) discloses aqueous liquid compositions comprising salting-out resistant surfactant material and optionally ethoxylated fatty alcohol.

EP 623670 (Albright & Wilson) discloses aqueous structured liquid compositions comprising a stabiliser polymer. The liquids contain nonionic surfactants with a low number of ethoxylate groups and high levels of non-soap anionic surfactants. The liquids may contain nonionic surfactants with high soap levels. EP 691399 (Colgate) discloses aqueous lamellar structured liquid detergent compositions comprising a stabiliser polymer.

WO 91/00331 (Unilever) discloses aqueous lamellar structured liquid compositions comprising a particular combination of two types of nonionic surfactants in order to provide for stability. Example 12 discloses a composition which comprises an ethoxylated Dobanol glycerol compound as stabilising nonionic surfactant.

WO 91/05844 discloses aqueous lamellar structured liquid compositions comprising particular ratios of nonionic surfactants and soap. The liquid pH is high. WO 91/08280 discloses aqueous lamellar structured liquid compositions comprising nonionic surfactant, soap and anionic surfactants. WO 91/09108 discloses aqueous lamellar structured liquid compositions comprising nonionic surfactant, soap and high levels of anionic surfactants.

Patent application PCT/EP95/03859 (Unilever) discloses aqueous liquid detergent compositions comprising high nonionic levels. The liquids contain nonionic surfactants with a low number of ethoxylate groups. The lamellar structured liquids comprise droplets with an asymmetric lamellar structure. We have found that these liquids may suffer from physical instability and phase separation, in particular upon storage at higher temperatures.

Generally, liquids with nonionic surfactants, in particular at higher levels, suffer from physical instability and high viscosity and they often require non-functional or undesirable stabilising materials.

In addition, we have found that aqueous liquids comprising a low nonionic:soap weight ratios may suffer from high viscosity, which causes pourability problems. These liquids may further suffer from odour problems and discoloration on storage at elevated temperature. Furthermore, we have found that particular nonionic surfactants may not have a positive performance and environmental profile.

Surprisingly, we have found that one or more of the above problems can be overcome.

Definition of the invention

The present invention relates to aqueous liquid detergent composition comprising symmetric lamellar droplets of surfactant material, wherein the surfactant comprises soap and nonionic surfactants, wherein the nonionic surfactants comprise alkoxylated nonionic, wherein the alkoxylated nonionic is of the formula R-O-(CnH2n-O)xH wherein R is alk(en)yl, n is from 2 to 4 and x is on average between 3 and 7 and wherein the weight ratio nonionic:soap is between 50:50 and 90:10.

The present invention further relates to a process of preparing an aqueous liquid detergent composition comprising nonionic surfactants soap, by simultaneously adding the surfactants to an aqueous electrolyte solution.

We have found that the liquids of the invention are stable and have a low viscosity.

Lamellar structured liquids

A preferred form of lamellar structures are lamellar droplets of surfactant material. The dispersed structuring phase in such liquids is generally believed to consist of an onion-like configuration comprising concentric bilayers surfactant molecules, between which water or an electrolyte solution is trapped, the aqueous phase. Liquids with a lamellar droplets structure are preferred as systems in which such droplets are close-packed provide a very desirable combination of physical stability and solid-suspending properties with useful flow properties, i.e. low viscosity with stability. Such liquids have for example been described in A. Jurgens, Microstructure and Viscosity of Liquid Detergent, Tenside Surfactants Detergent 26 (1989) 222 and J.C. van de Pas, Liquid Detergents, Tenside Surfactants Detergents 28 (1991) 158.

The presence and identity of a surfactant structuring system in a liquid may be determined by means known to those skilled in the art for example, optical techniques, various rheometrical measurements, X-ray or neutron diffraction, and sometimes, electron microscopy.

Contrary to the asymmetric liquids described in Patent application PCT/EP95/03859 (Unilever) and EP 623670 (Albright & Wilson), the present invention relates to liquids comprising symmetric lamellar droplets of surfactant material. Such symmetric lamellar droplets are fully concentrically lamellar droplets of bi-layers of surfactant material.

Surfactants

Soap & nonionic surfactant

Liquid compositions according to the invention comprise soap. Preferably, the soap is selected from acids having from 12 to 18 carbon atoms, for example oleic acid, ricinoleic acid, alk(en)yl succinate for example dodecyl succinate, and fatty acids derived from castor oil, rapeseed oil, groundnut oil, coconut oil, palmkernel oil or mixtures thereof. The sodium or potassium soaps of these acids can be used. Most preferably, the soap is unsaturated and in particular preferred is oleic acid.

The nonionic surfactants in the liquids according to the present invention comprise alkoxylated nonionic surfactants, wherein the alkoxylated nonionic is the formula R-O-(CnH2n-O)xH wherein R is alk(en)yl, n is from 2 to 4 and x is on average between 3 and 7.

Preferably, R is on average C9-14 alkyl, more preferably on average C10-13 alkyl, most preferably C10-12 alkyl.

The average ethoxylate groups content of the nonionic surfactant (x in the above formula) is determined by calculating the number average. Preferably, x is 4 or higher and 6 or lower.

Preferably, the nonionic has a hydrophobic chain with a degree of branching more than 15%, more preferably more than 35%. The degree of branching represents the percentage of molecules with a side chain. We have found that use of these branched nonionics leads to liquids which are more stable.

Preferably, the nonionic of the present invention is selected from Vista 1012-55, Lutensol AO5, Dobanol 1-5, Softanol 70, Synperonic 7, Dobanol 25-7 and Imbentine AG/124/75, and more preferably from Vista 1012-55, Lutensol AO5 and Dobanol 1-5.

We have found that these nonionic surfactants have high cleaning power in combination with an acceptable environmental profile. However, blends of ethoxylated nonionic surfactants with other nonionic surfactants may not meet the performance and environmental requirements. Preferably, liquids of the invention comprise less than 30%, more preferably less than 20, most preferably less than 10, especially preferred less than 5% by weight of C13-15 alcohol with 1-3 ethoxy groups. They are e.g. substantially free of such nonionics.

We have found that a particular weight ratio of nonionic surfactants:soap provides stable and low viscous liquids with high cleaning power. The weight ratio of nonionic surfactant:soap is from 50:50 to 90:10, preferably higher than 55:45, more preferably 60:40 and preferably lower than 80:20, most preferably lower than 75:25.

Preferably, the level of soap is from 2 to 20%, more preferably from 3 to 15%, most preferably from 5 to 10% by weight of the composition.

Preferably, the level of nonionic surfactant is more than 10% and lower than 40%, more preferably from 15 to 30%, most preferably from 18 to 25% by weight of the composition.

Preferably, the combined level of soap and nonionic surfactant is from 75 to 100%, more preferably from 80 to 100% and most preferably from 85 to 100%, especially preferred from 90 to 100%, for example from 95 to 100% by weight of the total surfactant. It is in particular preferred that the composition are substantially free from other surfactant material.

Preferably, the combined level of soap and nonionic surfactant is from 10 to 50%, more preferably from 15 to 40%, most preferably from 20 to 35% by weight of the composition.

Other surfactants

Compositions of the invention may comprise surfactant material other than soap and the nonionic surfactant of the present invention.

In the widest definition the surfactant material in general, may comprise one or more surfactants, and may be selected from anionic, cationic, nonionic, zwitterionic and amphoteric species, and (provided mutually compatible) mixtures thereof. For example, they may be chosen from any of the classes, sub-classes and specific materials described in 'Surface Active Agents' Vol.I, by Schwartz & Perry, Interscience 1949 and 'Surface Active Agents' Vol.II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in 'Tensid-Taschenbuch', H.Stache, 2nd Edn., Carl Hanser Verlag, München & Wien, 1981.

Although not preferred in view of processing complexity, liquid composition of the invention may optionally comprise further nonionic surfactants. These include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example acids, amides or alkyl phenols with alkyl oxides, especially ethylene oxide, either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C_6-C_{18}) primary or secondary linear or branched alcohols made by condensation of ethylene oxide with the reaction products of ethylene-diamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

Compositions of the present invention may optionally comprise anionic surfactant ingredients. Suitable anionic surfactants are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic surfactant compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C_8-C_{18}) alcohols produced, for example, from tallow or coconut oil, sodium and potassium alkyl (C_9-C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10}-C_{15}) benzene sulphonates; sodium alkyl glycerol ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_8-C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralized with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_{8-20}) with sodium bisulphite and those derived from reacting paraffins with SO_2 and Cl_2 and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10}-C_{20}

alpha-olefins, with SO_3 and then neutralizing and hydrolysing the reaction product. The preferred anionic surfactant compounds are sodium (C_{11}-C_{15}) alkyl benzene sulphonates and sodium (C_{16}-C_{18}) alkyl sulphates.

Also possible is the use of salting out resistant active materials such as for example described in EP-A-0,328,177, especially the use of alkylpolyglycoside surfactants such as for example disclosed in EP-A-0,070,074. Also alkyl mono glucosides may be used. Further, alkyl glucose ether may be used and/or polyhydroxy fatty acid amides as described in WO 92/06157, more particular the amides used in the Examples thereof.

Preferably, the total level of surfactants is at least 10% by weight of the composition, more preferred at least 15% by weight, most preferably at least 20% by weight of the composition; and preferably at most 60% by weight, more preferably at most 50%, most preferably at most 40% by weight of the composition, in particular preferred at most 32% by weight, for example at most 30% by weight of the composition.

We have found that it is useful to lower the level of a third surfactant in the composition in order to reduce complexity of the liquid in terms of processing and stability and/or to improve the environmental profile of the liquid. Therefore, it is preferred that the composition comprises e.g. less than 50%, preferably, less than 25%, more preferably less than 20%, most preferably less than 10% and in particular preferred substantially 0% by weight of other surfactants.

The liquids of the invention comprise nonionic surfactant and soap. Optionally further surfactants are present. These are preferably selected from primary alkyl sulphate, lineair alkyl benzene sulphonate, alkylethoxysulphates, sugar based surfactants (such as alkylglycosides and polyhydroxy fatty acid amides) and mixtures thereof.

Preferably, the ratio between the weight of the nonionic surfactant and the soap to the weight of the further surfactants is higher than 4:1, more preferably higher than 6:1, most preferably higher than 9:1 and in particular the composition is substantially free from other further surfactants.

Generally the level of non-soap anionic surfactant materials is from 0 to 10%. more preferred from 0 to 5%, most preferably from 0 to 3% by weight of the composition.

Electrolyte material

Compositions according to the invention comprise electrolyte material, some or all of which may be builder material.

Preferably the total level of electrolyte is from 1 to 60% by weight of the composition, more preferably from 5 to 45% by weight, most preferably from 10 to 30% by weight.

Preferably the level of dissolved electrolytes is from 1 to 45% by weight of the composition, more preferably from 5 to 35% by weight, most preferably from 10 to 25% by weight.

It is noted that for the purpose of the invention, the term electrolytes including builder material.

Preferably the level of non-soap builder material is from 5 to 40 % by weight of the composition, more preferred from 5 to 25 % by weight of the composition.

Compositions according to the invention preferably contain a salting-out electrolyte that is able to bring about internal structuring of the liquid, preferably in the form of lamellar droplets of the surfactant material. Salting-out electrolyte has the meaning ascribed to in specification EP-A-0,079,646, i.e. salting-out electrolytes have a lyotropic number of less than 9.5, preferably less than 9.0. Examples are sulphate, citrate, NTA and carbonate. Optionally, some salting-in electrolyte (as defined in the latter specification) may also be included. Preferably the compositions contain from 1% to 60%, especially from 10 to 45% of salting-out electrolyte.

Builder material

In any event, it is preferred that compositions according to the present invention include detergency builder material, some or all of which may be electrolyte. In this context it should be noted that some surfactant materials such as for example soaps, also have builder properties.

Examples of phosphorous containing inorganic detergency builders include the water-soluble salts, especially alkali metalpyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates. Phosphonate sequestrant builders may also be used. It may however be preferred to minimise the amount of phosphate builders.

Examples of non-phosphorus-containing inorganic detergency builders, when present, include water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites.

Examples of organic detergency builders, when present, include the alkaline metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates and polyhydroxysulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids, CMOS, tartrate

mono succinate, tartrate di succinate and citric acid. Citric acids or salts thereof are preferred builder materials for use in compositions of the invention.

In the context of organic builders, it is also desirable to incorporate polymers which are only partly dissolved, in the aqueous continuous phase as described in EP-A-0,301,882. This allows a viscosity reduction (due to the polymer which is dissolved) whilst incorporating a sufficiently high amount to achieve a secondary benefit, especially building, because the part which is not dissolved does not bring about the instability that would occur if substantially all were dissolved. Typical amounts are from 0.5 to 4.5% by weight.

It is further possible to include in the compositions of the present invention, alternatively, or in addition to the partly dissolved polymer, yet another polymer which is substantially totally soluble in the aqueous phase and has an electrolyte resistance of more than 5 grams sodium nitrilotriacetate in 100 ml of a 5% by weight aqueous solution of the polymer, said second polymer also having a vapour pressure in 20% aqueous solution, equal to or less than the vapour pressure of a reference 2% by weight or greater aqueous solution of polyethylene glycol having an average molecular weight of 6000; said second polymer having a molecular weight of at least 1000. Use of such polymers is generally described in our EP-A-0,301,883. Typical levels are from 0.5 to 4.5% by weight.

Deflocculating polymers

Deflocculating polymers have been described in the art. EP 346,995 (Unilever) describes deflocculating polymers having a hydrophillic backbone and one or more hydrophobic side-chains.

WO 91/06622 (Unilever) describes deflocculating polymers consisting of alternating hydrophobic and hydrophillic groups. WO 91/06623 (Unilever) describes deflocculating polymers consisting of nonionic monomers and ionic monomers. GB-A-2,237,813 (Unilever) describes deflocculating polymers consisting of a hydrophobic backbone and one or more hydrophillic side-chains. WO 93/01884 (Unilever) discloses deflocculating polymer having a ketone group. EP 623670 (Albright & Wilson) describes particular stabilising polymers. The document further discloses asymmetric lamellar structures. EP 691399 (Colgate) discloses aqueous lamellar structured liquid detergent compositions comprising a stabiliser polymer. WO 91/09109 (Unilever) discloses liquid detergent compositions comprising deflocculating polymers that are biodegradable and EP 703243 (Unilever) describes a process for preparing deflocculating polymers.

Surprisingly, we have found that incorporation of a deflocculating polymer in liquids of the invention with the particular nonionic surfactants and with the particular nonionic surfactant:soap ratio leads to good physical stability and to viscosity improvements. Consequently, composition of the invention preferably also comprise a deflocculating polymer. Deflocculating polymer of the present invention are preferably selected from:

1) polymers having a hydrophillic backbone and one or more hydrophobic side-chains. Preferably, the hydrophillic backbone comprises monomers selected from unsaturated C1-6 acids, ethers, alcohols, aldehydes or esters, sugar units, alkoxy units, maleic anhydride and saturated polyalcohols such as glycerol and the hydrophobic sidechains comprise C4-C20 alkyl and/or alkenyl chains. The hydrophilic groups may be linked to the hydrophobic groups by any possible chemical link, although the following types of linkages are preferred: -C-O-, -CO-O-,-C-C-, -C-N-,-CO-N-, -PO(OH)- or - O-.

2) polymers consisting of alternating hydrophobic and hydrophillic groups. Preferably, the hydrophobic groups comprises monomers selected from unsaturated C1-6 acids, ethers, alcohols, aldehydes or esters, sugar units, alkoxy units, maleic anhydride and saturated polyalcohols such as glycerol and the hydrophillic groups are selected from saturated and unsaturated alkyl chains, e.g. having from 5 to 24 carbon atoms. The hydrophilic groups may be linked to the hydrophobic groups by any possible chemical link, although the following types of linkages are preferred: -C-O-, -CO-O- or -O-.

3) Polymers consisting of nonionic monomers (A) and ionic monomers (B). Preferably, the ionic and nonionic monomers are selected from ethylenically unsaturated amides (such as acrylamide, methacrylamide and fumaride) and their N-substitued derivatives (such as N-(dimethyl amino ethyl)acrylamide), vinyl alcohol, vinyl acetate, vinyl heterocyclic amides (such as vinyl pyrrolidone), acrolein, allyl alcohol, hydroxy ethyl (meth) acrylate, hydroxy propyl (meth)acrylate, sugar units (such as saccharides and glucosides), glycerol and other polyalcohols. Further, they are selected from ethylenically unsaturated carboxylic acids, dicarboxylic acids such as acrylic acid, maleic acid, methacrylic acid, itaconic acid, fumaric acid, crotonic acid, aconitic acid and citraconic acid. Furthermore, they are selected from amino alkyl esters of unsaturated carboxylic acids such as 2-amino ethyl (metha)crylate, dimethyl amino ethyl (meth)acrylate, diethyl amino ethyl (meth)acrylate, dimethyl amino methyl (meth) acrylate, diethyl amino ethyl (meth)acrylate, vinyl or alkyl amines such as vinyl pyridine, vinyl morpholine or allylamine. The degree of ionisation of a monomer may be dependent on the circumstances in the product, e.g. the liquid pH. Preferably the amount of ionic monomers in the polymer is from 0.1 to 50 % by weight of the polymer, more preferred from 1 to 25%, most preferred from 4 to 15%.

4) polymers consisting of a hydrophobic backbone and one or more hydrophillic side-chains. Preferably, the hydrophobic backbone consists of monomers selected from polysiloxanes, polybutylacrylate, saturated and unsaturated C5-24 alkyl chains and polyoxyalkylene groups comprising from 4 to 50 propylene oxide and/or butylene oxide groups. Optionally, the hydrophobic monomers are bonded to the adjacent hydrophilic groups via an alkoxylene or polyoxyalkylene linkage, for example a polypropoxy or butyloxy linkage having from 1 to 50 alkoxylene groups. Preferably, the hydrophillic sidechains comprise groups selected from polyethoxy groups (preferably comprising from 4 to 50 ethylene oxide groups), polyglycerol, condensation polymers of polyglycerol and citric acid anhydride and condensation polymers of alpha-hydroxy acids or polyacetals. The hydrophilic groups may be linked to the hydrophobic groups by any possible chemical link, although the following types of linkages are preferred: -C-O-, -CO-O- or -O-.

5) polymers comprising a hydrophillic backbone and one or more alkyl sidechains (EP 623670). Preferably, the hydrophillic backbone comprises monomers selected from polyelectrolyte groups, polyglycoside groups, polyvinylalcohol group or polyvinyl pyrrolidone groups. The alkyl sidechain is preferably linked to the hydrophillic backbone by way of an -O-, -COO-, -S-, -NR1-, -PO4-R1 or - PO3-R1 groups, wherein R1 is H or C1-4 alkyl. Preferred polymers according to this subgroup are polyelectrolyte stabilisers of formula: R-X-(CZ2-CZ2)nH, wherein R is C5-25 alkyl, wherein at least one Z represents a carboxylate group COOM, where M is H or a metal or base, any other Z being H or a C1-4 alkyl group and N=1-100. The alkyl sidechain can be linked to the hydrophillic backbone as indicated above.

6) mixtures thereof.

The deflocculating polymer is preferably used at levels of from 0.01 to 5% by weight of the composition, more preferably from 0.1 to 2%, especially preferred from 0.5 to 1.5%.

Preferably, the compositions are substantially free of the nonionic polyhydroxy stabilising agent which contains 1 or 2 pentose or hexose sugar units, as described in Patent application PCT/EP95/03859 (Unilever).

Optional ingredients

Apart from the ingredients already mentioned, a number of optional ingredients may also be present, for example lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach precursors, chlorine-releasing bleaching agents such as trichloroisocyanuric acid, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases, amylases and lipases (including Lipolase (Trade Mark) ex Novo), enzyme stabilizers, anti-redeposition agents, germicides and colorants. Obviously in selecting the materials other than the polymer for use in compositions of the invention, also biodegradable materials are preferred for environmental reasons.

Liquid compositions

Liquid compositions of the invention preferably have a viscosity of less than 2,500 mPas at 21 s-1, more preferred less than 1,500 mPas, most preferred less than 1,000 mPas and preferably higher than 100, more preferably higher than 500 mPas at 21 s-1.

Liquid compositions according to the invention are physically stable. In the context of the present invention, physical stability for these systems can be defined in terms of the maximum separation compatible with most manufacturing and retail requirements. That is, the 'stable' compositions will yield no more than 10%, preferably no more than 5 %, most preferred no more than 2%, utmost preferred substantially 0% by volume phase separation, as evidenced by appearance of 2 or more separate phases when stored at 25°C for 21 days from the time of preparation.

Preferably the compositions of the present invention are concentrated. Therefore, the water level in the liquid detergent compositions according to the present invention is preferably at least 10%, more preferably at least 20%, most preferably at least 30% by weight of the composition and preferably at most 60% by weight, more preferably at most 50%, most preferably at most 40% by weight of the composition.

Preferably, the pH of the composition is lower than 12.0, more preferably lower than 10.0, most preferably lower than 9.0 and preferably higher than 7.0.

Process of preparing

Liquid compositions of the invention may be prepared by any conventional method for the preparation of liquid detergent compositions.

However, we have found a method that provides structured aqueous liquid detergent composition comprising nonionic surfactants and soap that shows physically stable and robust formulations of low viscosity.

Accordingly, a further embodiment of the present invention relates to a method of preparing a structured aqueous liquid detergent composition comprising nonionic surfactants and soap, by simultaneously adding the surfactants to an aqueous electrolyte solution.

We have found that in the preferred method of the invention provides the best molecular mix of the surfactant is assured, e.g. in the lamellar droplet phase. In addition, aging problems, such as phase separation and viscosity drifts, are limited.

Preferably, the nonionic and the soap are added in the form of a premix. Although not preferred, a third (or further) surfactant may be present in the composition and may preferably be added to the electrolyte solution simultaneously, e.g. in the form of a premix with other surfactants, such as the nonionic surfactant.

Preferably, one nonionic surfactant is used for the preparation of the liquid detergent, in order to decrease processing complexity.

Preferably, the surfactants are added to the electrolyte solution in the form of a mixture comprising less than 20% by weight of water, preferably less than 10% and more preferably being substantially free from water.

The preferred method for example involves the dispersing of the electrolyte ingredient(s) together with the minor ingredients, except for the temperature and pH sensitive ingredients such as enzymes, perfumes, etc -if any- in water of elevated temperature, followed by the addition of the builder material -if any-, the surfactant material(s) as a premix under stirring and thereafter cooling the mixture and adding any temperature and pH sensitive minor ingredients. The surfactant premix preferably contain all the anhydrous surfactant materials.

The deflocculating polymer may for example be added after the electrolyte ingredient or as the final ingredient. Preferably the deflocculating polymer is added prior to the formation of the lamellar structure.

The following examples illustrate the present invention.

Examples

Table 1 presents the effect of nonionic and soap on the physical stability of aqueous liquids.

Table 1 (nonionics are explained in Table 2).

Component	Ex. 1	Ex. 2	Ex. 3	Ex. 4a	Ex. 4b	Ex. 5a	Ex. 5b	Ex. 6a	Ex. 6b	Ex. 7a	Ex. 7b
Nonionic	26.4 (1)	26.4 (2)	19.8 (3)	19.8 (4)	19.8 (4)	19.8 (5)	19.8 (5)	19.8 (6)	19.8 (6)	19.8 (7)	19.8 (7)
Oleate	6.6	6.6	13.2	13.2	13.2	13.2	13.2	6.6	6.6	13.2	13.2
PAS#	0	0	0	0	0	0	0	6.6	6.6	0	0
Citrate	16.5	16.5	16.5	16.5	16.5	16.5	16.5	16.5	16.5	16.5	16.5
Defloc-culating polymer*	1	1	1	1	2	1	2	1	2	1	2
Water	rest	rest	rest	rest	rest	rest	rest	rest	rest	rest	rest
Definition lam droplets	sym-metric	sym-metric	sym-metric	poor	sym-metric	poor	sym-metric	poor	sym-metric	poor	sym-metric
Physical stability	stable	stable	stable	un-stable	stable	un-stable	stable	un-stable	stable	un-stable	stable

PAS means Primary Alkyl Sulphate
*Defloc. polymer is polymer A11 of EP 346995
The pH of the liquids is about 8.5.
It can be concluded that the preferred nonionic types decreases in the order 1) to 7), while nonionic types 1) to 3) are the most preferred types.

Table 2 is based on the liquids of table 1 and presents the effect of nonionic type on the maximum level of nonionic surfactant and deflocculating polymer to be included in liquid compositions in order to arrive at physically stable liquid detergent compositions with symmetric lamellar droplets.

Table 2

Non-ionic type	Nonionic Structure	Maximum amount of nonionic (as % of total surfactants) allowed to maintain symmetric lamellar droplets	% Primary Alkyl Sulphate (as % of total surfactants) needed for obtaining symmetric lamellar droplets	% deflocculating polymer necessary for physical stability
1) Vista 1012-55	C10-12, 0% branched 4.5EO	at least 80%	0	1
2) Lutensol AO5	C13-15, 39% branched 5EO	80%	0	1
3) Dobanol 1-5	C11, 15% branched 5EO	at least 60%	0	1
4) Softanol 70	C12-14, 100% branched 7EO	at least 60%	0	>1
5) Synperonic 7	C13-15, 35% branched 7EO	at least 60%	0	>1
6) Dobanol 25-7	C12-15, 18% branched 7EO	60%	20	>1
7) Imbentine AG/124/75	C12-14, 0% branched 7.5EO	at least 60%	0	>1

The preferred nonionic types decreases in the order 1) to 7), whilst nonionic types 1) to 3) are most preferred.

Table 3 presents liquid detergent compositions comprising soap, nonionic surfactant and optionally lineair alkyl benzene sulphonate.

Table 3

Component	Ex. 8	Ex. 9a	Ex. 9b
Nonionic	26.4 (1)	13.2 (5)	13.2 (5)
Oleate	6.6	13.2	13.2
LAS	0	6.6	6.6
Citrate	16.5	16.5	16.5
Deflocculating polymer	1	1	2
Water	rest	rest	rest
Definition lamellar droplets	symmetric	poor	symmetric
Physical stability	stable	unstable	stable
Deflocculating polymer is polymer A11 of EP 346995 LAS represents Lineair Alkyl benzene Sulphonate (Marlon AS3, ex Huls)			

Compositions in Table 1-3 have a sodium/potassium ratio of 1:1, on a molar base.

It can be concluded that the nonionic type 1) is preferred over 5) because Example 8:

a) does not need the third surfactant to stabilize the composition;

b) only needs 1% by weight of deflocculating polymer for stabilisation; and

c) the sample is much more rich in nonionic and gives a good performance.

In addition, liquids according to the examples comprising nonionic surfactants with a high number of ethoxylate groups (e.g. on average 11 EO) show a lower performance profile than the liquids with the nonionic surfactants of the present invention.

Table 4 presents complete formulations containing soap and nonionic surfactants.

Table 4:

Component	10	11	12	13	14	15	16	17	18	19
Nonionic	18 (1)	21 (1)	24 (1)	24 (1)	27 (1)	18 (6)	21 (6)	24 (6)	24 (6)	27 (6)
K-Soap	13.7	10.3	6.8	6.8	3.4	13.7	10.3	6.8	6.8	3.4
Glycerol	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Borax	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
K-Citrate	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4
Zeolite 4A (100%)	15	15	15	15	15	15	15	15	15	15
Defloc-culating polymer	1	1	1	2	2	1	1	1	2	2
Minors	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Permalose TM ex ICI(100%)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Water	rest	rest	rest	rest	rest	rest	rest	rest	rest	rest
Physical stability	stable	stable	border -line	stable	border -line	stable	border -line	un-stable	border -line	un-stable

It can be concluded that nonionic surfactant 1) is preferred over 6) because with nonionic 1):

a) stable liquid can be made which are richer in nonionic and b) less deflocculating polymer is required for stabilisation.

Claims

1. Aqueous liquid detergent composition comprising symmetric lamellar droplets of surfactant material, wherein the

surfactant comprises soap and one or more alkoxylated nonionic surfactants, each having the formula R-O-(CnH2n-O)xH, wherein R is C9-14 alk(en)yl, n is from 2 to 4 and x is on average more than 3 and less than 7 and wherein the weight ratio of alkoxylated nonionic surfactant to soap is between 50:50 and 90:10.

2. Composition according to claim 1, wherein the combined level of soap and nonionic surfactant is from 75 to 100% by weight of the total surfactant.

3. Composition according to claims 1-2, wherein R has a degree of branching of more than 15%, preferably more than 35%.

4. Composition according to claims 1-3, wherein the soap is unsaturated, preferably the soap is oleate.

5. Composition according to claims 1-4, wherein the weight ratio alkoxylated nonionic:soap is from 55:45 to 80:20.

6. Composition according to claims 1-5, wherein the surfactant level is from 10 to 60% by weight of the composition.

7. Composition according to claims 1-6, wherein the composition further comprises from 0.01 to 5% by weight of a deflocculating polymer.

8. Composition according to claims 1-6, wherein the water level is from 10 to 60% by weight of the composition.

9. Process of preparing an aqueous liquid detergent composition comprising nonionic surfactants, soap and electrolyte material, by simultaneously adding the surfactants to a solution of the electrolyte.

10. Process according to claim 9, wherein the surfactants are added to the electrolyte solution in the form of a mixture comprising less than 20% by weight of water.